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Local structure and optical absorption of Mn^{2+} doped Cs_2SO_4 single crystals

Maroj Bharati [1], Vikram Singh [1] and Ram Kripal [2,*]

[1] *Department of Physics, Faculty of Science, Nehru Gram Bharti University, Jamunipur, Prayagraj-221505, India*
[2] *Electron Paramagnetic Resonance Laboratory, Department of Physics, Faculty of Science, University of Allahabad, Prayagraj-211002, India*

* *Corresponding author at: Electron Paramagnetic Resonance Laboratory, Department of Physics, Faculty of Science, University of Allahabad, Prayagraj-211002, India.*
e-mail: ram_kripal2001@rediffmail.com (R. Kripal).

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ABSTRACT

Using perturbation theory and the superposition model, the splitting parameters for the zero field of Mn^{2+} doped crystals of Cs_2SO_4 are determined. When the local distortion is included in the computation, the estimated parameters match fairly well with the experimental ones. Theoretical evidence corroborates the experimental finding that the Mn^{2+} ion substitutes at the Cs^+ site in Cs_2SO_4. The crystal's optical spectra are computed by the diagonalization of a complete Hamiltonian in the coupling scheme of the intermediate crystal-field, using the crystal field parameters obtained from the superposition model and the crystal field analysis program. The calculated and experimental band positions agree fairly well. Consequently, the results of the experiment are confirmed by theoretical analysis.

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1. Introduction

The technique of electron paramagnetic resonance (EPR) can be used to ascertain the energies of transition metal ions' as they go through Zeeman transitions. The Mn^{2+} ion is the most studied transition ion, as it gives the EPR lines even at room temperature. It has a $3d^5$ electronic configuration and $^6S_{5/2}$ ground state. Its paramagnetism can be attributed only to the electron spin because it has zero angular momentum. Small structural changes in the crystal [1-5] show sensitivity to zero-field splitting in the crystals.

For use in EPR [6-9] and optical spectroscopy [10,11], the zero-field splitting (ZFS) and crystal field (CF) parameters can be modeled using the superposition model (SPM). The spin Hamiltonian (SH) is discussed together with other Hamiltonians in [12]. The parameters of the crystal field (CF) are often found using the SPM and the point-charge model [13] even if the exchange charge model (ECM) is also a useful technique for analyzing the effects of crystal fields in single crystals intoxicated with rare earth and transition ions [14]. In this study, we used SPM to calculate the ZFS parameters and the CF parameters. SPM was suggested [15] for CF based on the following assumptions: (i) An algebraic sum of the contribution of the crystal's other ions can be used to determine the paramagnetic ion's CF. (*ii*) All significant contributions to the conservation of free energy from each paramagnetic ion have axial symmetry with respect to their position vector when the ion is at the chosen coordinate system's origin. (*iii*) The CF contributions of just nearby or coordinated ions are to be taken into account. (*iv*) Across various host crystals, contributions to CF from a solitary ion (ligand) can be transmitted. The axial symmetry assumption, however, (*ii*) permits the transformation of one coordinate system into another; the first assumption provides support for the applicability of the superposition principle in characterizing the CF. Nonetheless, a more limited version of assumption (*iii*) is sometimes used, when solely the closest neighbor ions are occupied. According to the final ligand transferability assumption (*iv*), the only factors influencing the contributions of one ion to CF are its character and distance from the paramagnetic ion. To perform an SPM analysis on the CF, it is essential to obtain a steady polar coordinate system (R_L, θ_L, Φ_L) for each ligand or ion from the host crystal's X-ray data. When transition-metal ions are introduced, ionic size, ionic charge, and inter-ionic bonding mismatches will probably result in some degree of local distortion. To find the fitted values of the SPM power law exponents and the intrinsic parameters, a nonlinear or linear least squares fit may be performed on an adequate quantity of CF parameters. Mn^{2+} and Fe^{3+} experimental spin-Hamiltonian parameters in CaO and MgO crystals have been critically analy-

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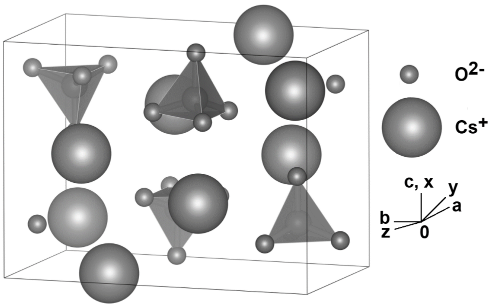

Figure 1. The symmetry-adopted axis system (SAAS) and the crystal structure of Cs_2SO_4 at room temperature.

zed [16]. For the EPR data, it gives the exact values of the SPM parameters and demonstrates that the superposition principle is satisfied by the CF for 3*d* ions. A strict lattice relaxation model was utilized [17] to determine sets of intrinsic parameters of the SPM based on reliable ligand distances for alkali earth oxides. For Fe^{3+} and Mn^{2+} doped MgO, CaO, and SrO (R_0 = 2.0 Å): $\bar{b}_2$ = -1552±48×10^{-4} cm^{-1} and -6440±113×10^{-4} cm^{-1}, respectively, with a fixed t_2 = 16 for both ions. For both Fe^{3+} and Mn^{2+}, the values of $\bar{b}_4$ are 9.9±0.8×10^{-4} cm^{-1}, with a fixed t_4 of 16±4 for each ion. The fitted values for Mn^{2+} and Fe^{3+}, respectively, were 17.7 and 14.4 for the separate fitting of t_2.

Cesium sulfate is a chemical compound that contains cesium and sulfur with formula Cs_2SO_4. For isopycnic centrifugation, dense aqueous solutions are made using this white, water-soluble solid. With potassium salt, it is isostructural. It is used in wastewater treatment and has high resistance to organic solvents, making it an experimental model for studying fatty acid degradation. This compound is used to study metal hydroxides and coordination geometry. Cesium sulfate is also used in biological samples such as plasma and human serum. It undergoes thermal expansion in the presence of light and emits light when heated to decomposition [18,19].

An EPR study of Mn^{2+} doped Cs_2SO_4 has been carried out in the temperature range of 77 to 293 K and spin Hamiltonian parameters of the system have been obtained [20]. According to angular variation studies, there is a complex where Mn^{2+} replaces a β-Cs^+ ion and associates with a nearby β-Cs^+ vacancy in the ab-plane along the complex's z-axis. It was discovered that the complex's *z*-axis and the crystal's *b*-axis form a 25° angle. The complex's *x*-axis runs along the crystal's *c*-axis, while its *y*-axis is in the same ab plane and is normal to the *z*-axis.

In the present study, the ZFS parameters D and E are determined for the Mn^{2+} ion in cesium sulfate at substitutional β-Cs^+ site at 293 K (room temperature, RT) using the CF parameters obtained from the SPM and perturbation equations [21]. The aim is to find the location of the Mn^{2+} ion and the distortion that occurs in the crystal. The results found for the Mn^{2+} ion at the substitutional β-Cs^+ site in the cesium sulfate crystal with local distortion provide a reasonable match with the experimental values. A further objective of the study is to obtain the extent to which CF theory and SPM analysis can be applied to Mn^{2+} ions in cesium sulfate crystals to create an SPM parameter database. Molecular nanomagnet (MNM) design and computer modeling of their magnetic and spectroscopic characteristics will be determined by this. Single-molecule magnets (SMM) [22], single chain magnets (SCM) [23], and single ion magnets (SIM) [24] are currently included in the transition-ion-based MNM class. The above systems have drawn a great deal of attention from researchers because of the noteworthy magnetic characteristics of MNM, for instance, magnetization's macroscopic quantum tunneling, and potential applications in quantum computing and high-density information storage [22,23]. There are many synthesized SCM or SMM systems with Mn^{2+}andCr^{3+} ions [25]. The parameters of the model established in this case may be used for ZFS parameter calculations for Mn^{2+} ions at similar sites in MNM, since model calculations for simpler crystal systems can serve as a foundation for more complex ones. The modeling utilized in this work can be extended to explore crystals of scientific and industrial interest in several other ion host systems.

2. Crystal structure

The crystal structure of cesium sulfate, isomorphous to potassium, ammonium, and rubidium sulfates, has been determined by Ogg [26]. The crystal belongs to the symmetry group D_{2h}^{16} and contains two reflection planes, four glide planes, twelve dyad screw axes, and sets of four centers of symmetry. The dimensions of the orthorhombic unit cell are *a* = 6.218, *b* = 10.884 and *c* = 8.198 Å. The structure of Cs_2SO_4 consists of layers of atoms parallel to the (100) planes, the spacing between which is *a*/2. The reflection planes are $(100)_{1/4}$ and $(100)_{-1/4}$, the origin of coordinates is assumed at the center of the unit cell. The unit cell contains four formula units. According to the oxygen environment, cesium atoms are classified as α- or β-type [19,26]. As a result, there are four cesium ions of α-type and four cesium ions of β-type in the unit cell. Figure 1 shows the crystal structure of cesium sulfate with the adopted symmetry axis system (SAAS).

3. Crystal field and zero field splitting parameter calculations

The analysis of EPR spectra is performed with the spin Hamiltonian (Equation 1) [7,8]:

$$\mu_B B.g.S + D\left\{S_Z^2 - \frac{1}{3}S(S+1)\right\} + E(S_x^2 - S_y^2) = \mathrm{H} \tag{1}$$

where B, μ_B, g, D and E are the applied magnetic field, Bohr magneton, splitting factor, second-rank axial and second rank rhombic ZFS parameters [27,28]. Crystal axes *a*, *b* and *c*, along with the laboratory axes (*x*, *y*, *z*), are shown in Figure 1. The directions of metal-ligand bonds that are mutually perpendicular are referred to as the local symmetry axes of the site or the symmetry-adopted axes (SAA). As demonstrated in Figure 1, the axis-*x* of SAAS is along the crystal axis-*c*, and (*y*, *z*) are perpendicular to the axis-*x*. When Mn^{2+} ions are doped into the Cs_2SO_4 crystal, they enter the lattice at substitutional β-Cs^+ sites with some local distortion [29].

For a 3d^5 ion, the spin Hamiltonian can be written as (Equations 2 and 3) [30],

$$\mathrm{H} = \mathrm{H}_0 + \mathrm{H}_{so} + \mathrm{H}_{ss} + \mathrm{H}_c \tag{2}$$

Table 1. Atomic coordinates, bond length R (both with and without distortion), and angles θ, φ in Cs_2SO_4 single crystal (site I) *.

Ligands	*x* (Å)	*y* (Å)	*z* (Å)	R (nm) (ND)	R (nm) (WD)	θ° (ND)	θ° (WD)	φ° (ND)	φ° (WD)
O1	0.250	0.417	0.067	0.13073	0.19286	87.06	88.26	90.00	91.50
O2	0.250	-0.455	0.311	0.86870	0.94870	87.95	89.95	90.00	92.00
O3	0.053	0.353	0.311	0.28706	0.46707	83.78	85.28	93.96	95.96
O4	0.553	0.147	0.189	0.30035	0.38035	86.39	94.39	84.20	90.20
O5	-0 .053	0.853	-0.311	0.67257	0.85758	92.65	94.65	92.58	92.58
O6	0.447	-0.353	0.811	0.98723	1.07223	85.28	85.28	88.85	90.85

* Substitutional: Mn (0.250, 0.308, 0.000), ND = No distortion, WD = With distortion.

Table 2. The Mn^{2+} doped Cs_2SO_4 crystal's crystal field and zero field splitting parameters *.

Site	R_0 (nm)	CF parameters (cm^{-1})					Zero-field splitting parameters		
		B_{20} (cm^{-1})	B_{22} (cm^{-1})	B_{40} (cm^{-1})	B_{42} (cm^{-1})	B_{44} (cm^{-1})	|D| ($\times 10^{-4}$ cm^{-1})	|E| ($\times 10^{-4}$ cm^{-1})	|E|/|D|
Site I ND	0.200	-24985.0	-30744.3	34177.26	36217.17	50793.73	29578.1	12285.6	0.415
Site I WD	0.200	-8970.37	7147.075	2294.573	2419.935	5629.302	879.3	227.5	0.258
						Exp.	879.3	13.1	0.015

* ND = No distortion $\frac{\bar{A}_2}{\bar{A}_4}$ = 10, WD = With distortion, $\frac{\bar{A}_2}{\bar{A}_4}$ = 10, $^{Exp.}$ = experimental.

$$H_c = \sum B_{kq} C_q^{(k)} \qquad (3)$$

where B_{kq}, in Wybourne notation, are the CF parameters and $C_q^{(k)}$ are the spherical tensor operators of Wybourne. $B_{kq} \neq 0$ in the orthorhombic symmetry crystal field only for k = 2, 4; q = 0, 2, 4. Using SPM, the CF parameters B_{kq} are calculated [31].

The symmetry of the local field about Mn^{2+} ions in the Cs_2SO_4 crystal is considered orthorhombic (OR-type I) [7]. In OR-type I symmetry, the ZFS parameters D and E are established as follows (Equations 4 and 5) [31]:

$$D = \left(\frac{3\varsigma^2}{70P^2D'}\right)\left[-B_{20}^2 - 21\varsigma B_{20} + B_{22}^2\right] + \left(\frac{\varsigma^2}{63P^2G}\right)\left[-5B_{40}^2 - 4B_{42}^2 + 14B_{44}^2\right] \qquad (4)$$

$$E = \left(\frac{\sqrt{6}\varsigma^2}{70P^2D'}\right)\left[2B_{20} - 21\varsigma\right]B_{22} + \left(\frac{\varsigma^2}{63P^2G}\right)\left[3\sqrt{10}B_{40} + 2\sqrt{7}B_{44}\right]B_{42} \qquad (5)$$

In the above equations, P = 7B + 7C, G = 10B + 5C, D' = 17B + 5C. B and C are the Racah parameters and ς are the spin-orbit coupling parameter. With the average covalency parameter N in mind, we get $B = N^4B_0$, $C = N^4C_0$, $\varsigma = N^2\varsigma_0$, where ς_0 presents free ion spin-orbit coupling parameter and B_0 and C_0Racah parameters for free ion [30,32]. B_0 = 960 cm^{-1}, C_0 = 3325 cm^{-1} and ς_0 = 336 $cm^{-1}$for free Mn^{2+} ion [7].

The parameter N is evaluated from $N = \frac{1}{2}\left(\sqrt{\frac{B}{B_0}} + \sqrt{\frac{C}{C_0}}\right)$ taking the Racah parameters (B = 850 cm^{-1}, C = 2970 cm^{-1}) obtained from optical analysis of the Mn^{2+} ion in zinc cesium sulfate hexahydrate, the crystal with oxygen ligands [33], as there is no optical study of Mn^{2+} doped Cs_2SO_4 reported in the literature.

The CF parameters, in terms of co-ordination factor $K_{kq}(\theta_j, \phi_j)$ and intrinsic parameter $\bar{A}_k(R_j)$, using SPM are found [15,31] as in (Equation 6),

$$B_{kq} = \sum_j \bar{A}_k(R_j) K_{kq}(\theta_j, \phi_j) \qquad (6)$$

$\bar{A}_k(R_j)$ is provided by (Equation 7)

$$\bar{A}_k(R_0)\left(\frac{R_0}{R_j}\right)^{t_k} = \bar{A}_k(R_j) \qquad (7)$$

where the ligand's distance from the d^n ion is denoted by R_j, $\bar{A}_k(R_0)$ is the intrinsic parameter, R_0 is the reference distance of the ligand from the metal ion and t_k denotes power law exponent. For Mn^{2+}doped crystals, t_2 = 3 and t_4 = 7 are used [31].

Different values are considered in the present calculation, as discussed later. As the coordination about the Mn^{2+} ion is octahedral, $\bar{A}_4$ is found from the relation (Equation 8) [34],

$$\bar{A}_4(R_0) = \frac{3}{4}Dq \qquad (8)$$

From optical study [33], D_q = 790 cm^{-1}. Therefore, $\bar{A}_4(R_0)$ = 592.5 cm^{-1}. For $3d^5$ ions the ratio $\frac{\bar{A}_2}{\bar{A}_4}$ falls in the range 8-12 [30,35,36]. With $\frac{\bar{A}_2}{\bar{A}_4}$=10, $\bar{A}_2$ = 5925 cm^{-1}.

4. Results and discussion

Using SPM, parameters $\bar{A}_2$ and $\bar{A}_4$, and the ligand arrangement about Mn^{2+} ion as indicated in Figure 1, the CF parameters of the Mn^{2+} ion at the substitutional β-Cs^+ sites are calculated. Table 1 provides the atomic coordinates in the Cs_2SO_4 single crystal along with the bond length R (both with and without distortion) and angles θ, φ for site I. The CF parameters from Equation 6 and the ZFS parameters obtained using Equations 4 and 5 together with the reference distance R_0 are depicted in Table 2. Table 2 demonstrates that R_0 = 0.200 nm is somewhat less than the sum of radii of ions (0.223 nm) of Mn^{2+} = 0.083 nm and O^{2-} = 0.140 nm along with no distortion yield ZFS parameters for substitutional octahedral site I to be different from the experimental values [20]. Experimental ZFS parameter values |D| and |E| (in 10^{-4} cm^{-1}) for site I are 879.3, 13.1, respectively. |E|/|D| is found to be 0.015, which is quite smaller than the standard value 0.33 [28]. |D| and |E| determined theoretically without distortion are larger than the experimental values. The value of |E|/|D| is also larger than the standard value 0.33 [28]. Therefore, the local distortion is taken into account. Using the above value of R_0 and local distortion, the ZFS parameter |D| for substitutional octahedral sites I is in good accord with those from the experiment [20] but |E| value is larger than the experimental one. However, this gives |E|/|D| ratio close to the standard value [28]. Thus, the theoretical |E| value seems to be more appropriate. The parameters t_2 = 3 and t_4 = 7 with the transformation S2 for standardization [28] have been used to obtain |E|/|D| ratio< 0.33 and calculated ZFS parameters close to experimental values.

The CFA program [37] and B_{kq} parameters (with distortion) are used to calculate the Mn^{2+} doped Cs_2SO_4 single crystals' optical spectra. After diagonalization of the complete Hamiltonian, the positions of the energy bands of Mn^{2+} ions are determined. Table 3 displays the energy band positions for substitutional site I based on experimental and calculation data [33].

Table 3. The positions of the energy bands of the single crystal of Cs_2SO_4 doped Mn^{2+}, both calculated and experimental.

Transition from $^6A_{1g}(S)$	Observed wavenumber (cm^{-1})	Calculated wavenumber (cm^{-1})					
$^4T_{1g}(G)$	18436	20310	20315	20974	20997	22543	22581
$^4T_{2g}(G)$	22815	22997	23021	23351	23370	23673	23688
$^4E_g(G)$	24783	23866	23877	23929	23951	-	-
$^4A_{1g}(G)$	24850	24863	24865	-	-	-	-
$^4T_{2g}$(D	28003	26712	26757	27568	27586	27981	28004
$^4E_g(D)$	29870	28538	28575	29754	29820	-	-
$^4T_{1g}(P)$	32435	31232	32107	32391	32525	32580	32790
$^4A_{2g}(F)$	-	36562	36991	-	-	-	-
$^4T_{1g}(F)$	41460	40592	41107	41124	41313	41365	41510

Table 3 indicates that the calculated and experimental energy band positions agree fairly well. Therefore, the theoretical results corroborate the experimental finding [20,33] that Mn^{2+} ions enter the Cs_2SO_4 crystal at the substitutional octahedral site. The model parameters obtained here may be utilized in ZFS parameter estimations for Mn^{2+} ions at comparable MNM sites.

5. Conclusions

Zero field splitting parameters using perturbation theory and the superposition model for Cs_2SO_4 single crystals intoxicated with Mn^{2+} ions are estimated. The calculated ZFS parameters agree well with the experimental values. The calculated positions of the optical energy bands agree reasonably well with those obtained from the experiment. Therefore, the experimental result is supported by the theoretical analysis that Mn^{2+} ions occupy substitutional sites in Cs_2SO_4. The model parameters estimated in this study can be utilized for the calculation of the ZFS parameters for Mn^{2+} ions at comparable locations in molecular nanomagnets. The current modeling technique can be extended to explore crystals of numerous scientific and industrial applications.

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Disclosure statement DS

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Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

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Conceptualization: Ram Kripal, Vikram Singh; Methodology: Maroj Bharati, Vikram Singh; Software: Ram Kripal, Vikram Singh; Validation: Maroj Bharati, Vikram Singh; Formal Analysis: Maroj Bharati, Vikram Singh; Investigation: Maroj Bharati, Vikram Singh; Resources: Maroj Bharati, Vikram Singh; Data Curation: Maroj Bharati, Vikram Singh; Writing - Original Draft: Maroj Bharati, Vikram Singh; Writing - Review and Editing: Ram Kripal, Vikram Singh; Visualization: Vikram Singh, Ram Kripal; Funding acquisition: Vikram Singh, Maroj Bharati; Supervision: Ram Kripal; Project Administration: Ram Kripal.

ORCID and Email

Maroj Bharati
marojbharati99@gmail.com
https://orcid.org/0009-0007-8219-0993
Vikram Singh
vikram.singh@ngbu.edu.in
https://orcid.org/0000-0003-3813-586X
Ram Kripal
ram_kripal2001@rediffmail.com
https://orcid.org/0000-0002-3483-8704

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